

METHANOL AND HYDROGEN FROM METHANE, WATER, AND LIGHT

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Introduction

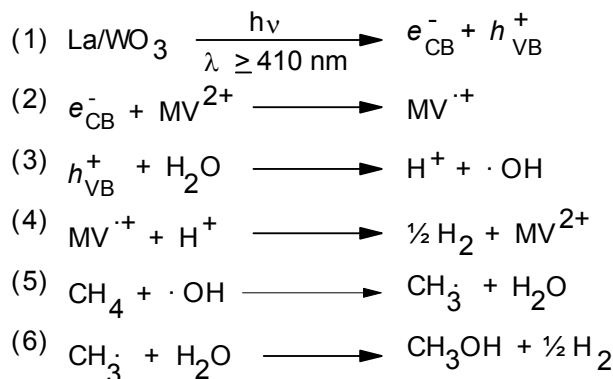
Research on the conversion of natural gas (methane) has been an ongoing effort at the National Energy Technology Laboratory (NETL) for over 20 years. A long-term goal of our research team is to explore novel pathways for the direct conversion of methane to liquid fuels, chemicals, and intermediates.

Literature reports have indicated that photochemical oxidation of methane may be a commercially feasible route to methanol [1, 2]. In these studies, methane, water and light are reacted at moderate temperatures and pressures.

Research in our laboratory [3] has shown that, methane, dissolved in water, at temperatures > 70 °C, with a semiconductor catalyst, can be converted to methanol and hydrogen. The use of three relatively abundant and inexpensive reactants - light, water, and methane - to produce methanol is an attractive process option. The main advantage of using a photocatalyst to promote the photoconversion of methane to methanol is that the presence of the catalyst, in conjunction with an electron transfer agent, allows reaction to occur with visible light instead of with ultraviolet. This greatly simplifies reactor design and will permit flexibility in the selection of the light source. The products of the reaction of interest, methanol and hydrogen, are both commercially desirable as fuels or chemical intermediates. The limiting factor for conversion of methane appears to be the solubility of methane in water. We hypothesized that if the concentration of methane in water can be increased, conversion should also increase. Methane hydrates might provide a method of increasing the amount of methane dissolved in water, because at standard temperature and pressure (STP), one volume of saturated methane hydrates contains approximately 180 volumes of methane.

Methane hydrates were first observed in the laboratory in 1810. It wasn't until nearly 150 years later that they were observed in nature. Hydrates can occur in permafrost, in sediment where gas exists under moderate to high pressure and low temperatures, and offshore beneath deep water. Hydrates are a problem in the oil and gas production industry because they can form in the well or pipelines, thereby blocking the flow of fuel. Estimates by the U.S. Geological Survey project that world hydrate deposits contain approximately 2×10^4 trillion cubic meters of methane [4]. Estimates of methane hydrate deposits off the coast of the United States is approximately 9×10^3 trillion cubic meters of methane with an additional 17 trillion cubic meters of methane in the permafrost on the north slope of Alaska [1].

Our vision is to immobilize methane and water in close proximity by formation of the methane hydrate. The reaction will involve the formation of hydroxyl radical ($\bullet\text{OH}$) within the methane hydrate by photochemical means. The proximity and restricted mobility of the $\bullet\text{OH}$ and the CH_4 would then favor the formation of CH_3OH . Successful demonstration of this principle would then open the possibility of using hydrates to immobilize reactants in a way that favors the desired selectivity. This is the basis of our Patent [5].



e_{CB}^- = electron in conduction band, h_{VB}^+ = positive hole in valance band

Scheme 1: Proposed pathway for the photocatalytic conversion of methane and water

EXPERIMENTAL

The tungsten oxide semiconductor photocatalysts were synthesized following a modification of the procedure in the literature [6]. Four dopants, copper, lanthanum, platinum, and a mixture of copper and lanthanum, were selected for study on the tungsten oxide catalyst base. The titania photocatalyst used in this study is a proprietary sol-gel TiO_2 catalyst obtained from Attia Corporation.

The 1.0 MPa, a commercially supplied 1-liter quartz photochemical reaction vessel, was fitted to meet the needs of this research. This included use of a Teflon-coated magnetic stirring bar in the reactor, a fritted glass sparger, a nitrogen line used to cool the UV lamp, and an injection port.

In a typical 1.00 MPa pressure experiment, the sintered catalyst is suspended, by mechanical stirring, in double-distilled water (~750 mL) containing an electron-transfer reagent, methyl viologen dichloride. A mixture of methane (5 mL/min) and helium (16 mL/min) is sparged through the photocatalytic reactor. The helium is an internal standard for on-line analysis of the reactor effluent. The reaction temperature is maintained at ~371 K by circulation of heated (~393 K) silicone oil in the outer jacket of the reactor. A high-pressure mercury-vapor quartz lamp is used as the light source.

All pressurized and hydrate reactions were conducted in a high-pressure view cell. The cell is constructed of 316 stainless steel 6.35 cm (2.5 inches) OD and 27.4 cm (11 inches) in length. The internal volume of the cell is ~40 mL. The cell is fitted with 2 machined endcaps, one which contains a sapphire window to allow for observation of the contents of the cell using a CCD camera. The cell is fitted with ports to accommodate the fill gas inlet and reaction product outlet, a pressure transducer to monitor the internal pressure of the gas inside the cell, and a thermocouple that terminates inside the cavity of the cell to monitor the temperature of the liquid/hydrate mixture. While the working pressure of the cell is rated at 220 MPa (32,000 psia), all experiments were conducted at 13.8 MPa (2000 psig) or less. The temperature of the cell is controlled by the flow of a glycol/water solution from an external circulating temperature bath through a coil of 0.64 cm (¼ inch) copper tubing that is wrapped around the outside of the cell. Several layers of insulating material are wrapped around the cell to help maintain constant temperature.

A typical experiment involves filling the cell with 40 mL of double-distilled water. A Teflon® coated stir bar is added, followed by portions of the photocatalyst. The endcap is placed on the cell and tightened to specifications. An external magnetic stirrer is used to obtain a high degree of vortex mixing inside the cell. The cell is connected to the gas manifold and purged several times with

methane. Following the purge procedure, the cell is charged with methane at pressures of 5.5 – 13.8 MPa (800-2000 psig). Using the external circulating temperature bath, the temperature of the water in the cell is lowered until formation of the methane hydrate is observed. After formation of the hydrate, the temperature of the cell is lowered to -5 °C and held constant. Illumination of the hydrate is then performed using a high-pressure 350-watt mercury-vapor lamp, with the light directed toward the sapphire window. After illumination for a set period of time, the cell is allowed to warm slowly to room temperature. When the cell and its contents have reached room temperature, the contents of the cell are vented and a gas chromatograph and/or a mass spectrometer are used to analyze the products.

RESULTS

Of the four-tungsten oxide (doped with platinum, lanthanum, copper, and a 50/50 molar mixture of copper and lanthanum) and the sol-gel titania catalysts studied, the tungsten oxide catalyst doped with lanthanum exhibited the largest methane conversion and methanol yield. This catalyst was the one chosen for use in this study (Figure 1).

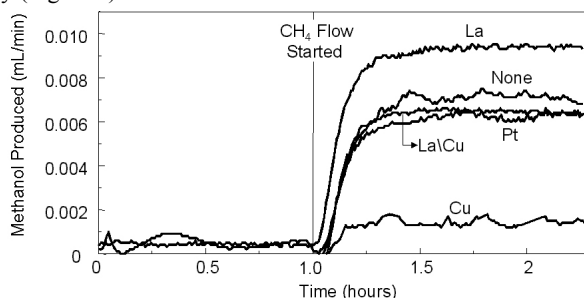


Figure 1. Methanol production with various promoted tungsten oxide photocatalysts.

Figure 2 shows the results of a typical photocatalytic methane conversion experiment at 1.0 MPa. Methane conversions are ~4% with hydrogen and methanol as the main products of reaction. Note that after the UV lamp is turned off, the detected flow of methanol decreases slowly to zero (over ~2 hours). It was hypothesized that this behavior was due to stripping of methanol from the water in the reactor by the reactant gases. To confirm this, methanol was injected into the reactor, previously filled with 750 mL water at the operating temperature, and the concentration of methanol in the gas flow from the reactor was measured as a function of time. A decrease in methanol concentration over several hours, similar to that observed in experiments undergoing methane photoconversion, was observed.

As noted previously, the proposed reaction sequence of interest initially produces hydroxyl radical, which then reacts with methane to produce methanol. To test the validity of this hypothesis, a 30% solution of hydrogen peroxide, a good source of hydroxyl radicals, was injected into the reactor during photocatalytic methane conversion. After peroxide injection, conversion of methane increases from ~4% to ~10%, methanol production increases 17 fold, and carbon dioxide increases 5 fold, along with modest increases in hydrogen and carbon monoxide. A drop in methane conversion to zero for approximately 12 min after injection of the hydrogen peroxide solution was observed in all experiments. This drop in methane conversion can be explained by assuming that prior to injecting hydrogen peroxide solution; a steady-state condition existed between the methane dissolving in the water and methane being consumed. It is likely that the introduction of excess hydroxyl radicals depleted the dissolved methane. At the temperature where the reactions were conducted, the solubility of methane in water is

very low (0.017 ml of methane per ml of water [7]). This low solubility results in little methane available for conversion until steady-state conditions could be re-established.

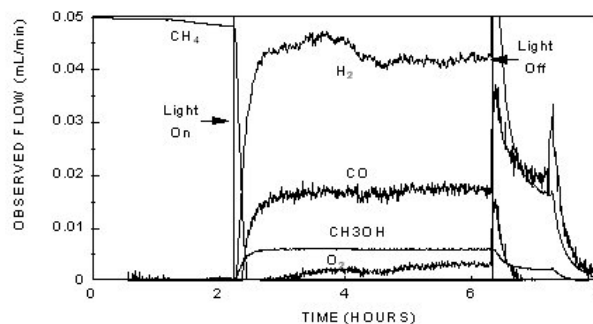


Figure 2. Products of the photocatalytic conversion of methane in water at 1.00 MPa and 370 K.

Note that in Figure 2, after the UV lamp is turned off, the detected flow of methanol decreases slowly to zero (over ~2 h). This is due to stripping of dissolved methanol from the water in the reactor by the reactant gases. Gas chromatographic analysis of the liquid product that had condensed in the trap at 273 K revealed the presence of methanol and acetic acid. Further analysis to identify other components by GC-MS was not possible due to the low concentration of products in the trap. The products were diluted by water carried over from the reactor in the flow of helium that is used as an internal standard.

The tungsten oxide photocatalyst is reported to function at wavelengths >410 nm. All results reported above were obtained using the UV lamp's total spectrum output. In order to separate reactions initiated by radiation with UV light from reactions initiated by visible light, a filter was constructed to block the UV portion of the lamp's energy output. The filter, a Pyrex ® sleeve fitted around the lamp, absorbs nearly all radiation below ~310 nm. The total energy output of the lamp with the filter in-stalled is ~50% of that without the filter. Experiments using the filter around the lamp were conducted under conditions described above. The results of experiments conducted with the UV filter installed gave similar conversions and product selectivities as those observed using the full spectrum of the lamp (Figure 3).

Photocatalytic conversion of methane and water at 10.1 MPa produced a product slate similar to that obtained at atmospheric pressure. What is of note is that while no conversion of methane was observed for the experiments conducted at atmospheric pressure at temperatures less than 343 K, at 10.1 MPa conversion occurred at 323 K.

The majority of the photocatalytic research, including the photocatalytic conversion of methane in methane hydrates, was performed with the lanthanum-promoted tungsten oxide photocatalyst. Figure 3 shows the results of photocatalytic conversion of methane dissolved in water at atmospheric pressure and 97°C for various dopants. As is shown, the catalyst doped with lanthanum out performs the other doped catalyst for the production of methanol.

Photocatalytic conversion of the methane contained within the methane hydrate molecule produced results similar to the two previously described experiments; methanol and hydrogen were the main products. This is an interesting result as at atmospheric pressure, no photocatalytic conversion of methane dissolved in water is observed at temperatures below 70°C. The photocatalytic conversions of the methane hydrate occurred at temperatures of -5°C and below.

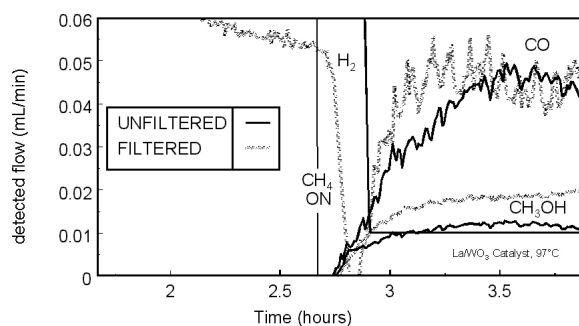


Figure 3. Products of the photocatalytic reaction of methane dissolved in water at atmospheric pressure and 97°C with full spectrum and filtered (visible) light.

Analysis, by mass spectrometry (Figure 4), of the gas contained in the headspace of the cell after illumination revealed the presence of methanol, hydrogen, ethane, oxygen, formic acid, and carbon dioxide. The formation of methanol and hydrogen are the primary products of reaction. The other products observed are formed by side reactions. Photocatalytic splitting of water (a side reaction not shown but observed in our laboratory when using this catalyst) forms oxygen. Ethane is formed by the combination of two methyl radicals (produced in Equation 5), and the formic acid and carbon dioxide are the result of further reactions of methanol.

The results of photocatalytic conversion of methane contained within methane hydrates with a sol-gel titanium dioxide photocatalyst are similar to the tungsten oxide photocatalyst with the exception that while methanol and hydrogen are produced by the reaction, oxygen is the main product of the titanium sol-gel photocatalyst.

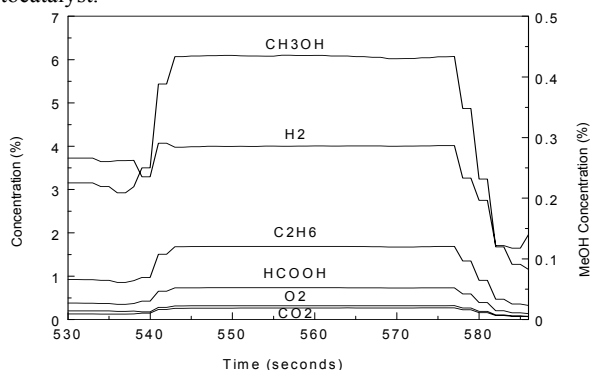


Figure 4. Products of the photocatalytic conversion of methane in methane hydrate with lanthanum-promoted tungsten oxide photocatalyst.

CONCLUSIONS

By use of a photocatalyst and electron-transfer reagent, we have been able to convert methane and water to methanol and hydrogen. Products of conversion at atmospheric pressure and 10.1 MPa were similar. While photoconversion of methane and water to methanol and hydrogen did not occur below 343 K at 1.0 MPa, conversion was observed at 323 K at 10.1 MPa and at temperatures as low as 258 K in methane hydrates. We also observe several side reactions of methane conversion in all instances, the production of ethane, oxygen, formic acid and carbon dioxide.

Under the conditions used in the 1 MPa experiments, the photocatalytic reaction produced 1.7 g of methanol-per gram of catalyst-per hour in the steady-state mode and produced 43 g of

methanol-per gram of catalyst-per hour when hydrogen peroxide solution was added.

The use of a filter removed the UV component from the lamp. Experimental results show that little difference between the filtered and unfiltered lamp was observed in the case of the platinum-doped tungsten oxide sample. This indicates that the photocatalyst is operating using visible light, the UV portion of the lamp's output is negligible in the photocatalytic conversion of methane to methanol, and that a limiting factor in conversion may be the solubility of methane in water.

In all experiments, conversion of methane and the production of methanol are augmented by the addition of hydrogen peroxide solution, consistent with the postulated mechanism that invokes a hydroxyl radical as an intermediate in the reaction sequence. The use of other radical initiators would be of interest to determine if the enhanced conversion could be sustained.

After the hydrate had formed and the pressure in the cell equilibrated, the UV lamp was turned on to initiate the photocatalytic conversion process. During illumination, a decrease in the pressure of the cell is observed. Following illumination, the cell was maintained at -2°C for several hours before warming to room temperature. Also of note is that the final pressure of methane is less than the starting methane pressure due to conversion of the methane within the hydrate.

Mass spectrometric analysis of the gas vented from the cell after illumination revealed the presence of methanol, hydrogen, ethane, oxygen, formic acid, and carbon dioxide, as shown in Figure 4. Side reactions that occur during the photocatalytic conversion process are responsible for producing these additional species. Photocatalytic splitting of water forms oxygen, ethane is formed by the combination of two methyl radicals, and the formic acid and carbon dioxide are the result of further reactions of methanol.

Attempts to use GC to identify products dissolved in the water after reaction were of limited value. In an effort to detect these products dissolved in the water, the cell and its contents were heated to 70°C prior to venting. Analysis of the gas headspace resulted in the detection of similar products as those obtained at room temperature. If products dissolved in the water were present, their concentration was too low to be detected with our setup. We are currently refining our detection system to correct this problem.

Experiments were also performed where the double-distilled water was replaced with simulated seawater. The results of these experiments were similar to those performed with double-distilled water.

DISCLAIMER. Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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